In the field of gas analysis, adsorbents offer the possibility of very selective separations that depend on the geometry of the molecules to be separated rather than the more generalized solubility mechanisms acting in gas–liquid chromatography. It should be theoretically possible to design adsorbents for particular separations. In the branch of liquid chromatography known as affinity chromatography, for example, it is already possible to manufacture stationary phases of exquisite specificity. An analogous approach might be possible in gas–solid chromatography and considerable work is in progress on the preparation and properties of molecular sieves with different dimensions to the well-established materials.

See also: **II/Chromatography: Gas:** Column Technology; Detectors: General (Flame Ionization Detectors and Thermal Conductivity Detectors); Historical Development; Theory of Gas Chromatography. **III/Gas Analysis: Gas Chromatography.**

Further Reading

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Headspace Gas Chromatography

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Introduction

The term 'headspace analysis' was first applied to the analysis of gases in sealed cans and was later applied to the general analysis of vapours in contact with the sample from which they come. Gas chromatography was the technique of choice for this type of analysis; the combination is therefore called *headspace–gas chromatography* (HS-GC).

For quantitative analysis calibration of the volatiles in the vapour is necessary. This is achieved preferably, but not necessarily, in a state of equilibrium. To reach this state the sample is placed in a glass vial and thermostatted. When equilibrium is achieved, an aliquot of the gas phase above the sample is rapidly transferred onto the GC column. The term *equilibrium HS-GC* is commonly used for this sampling technique. However, since under certain circumstances calibration for quantitative analysis may also be performed in a nonequilibrium system, the term *static HS-GC* is more appropriate to distinguish this sampling technique from the so-called *dynamic HS-GC* techniques. In dynamic HS-GC analysis, the volatile compounds are stripped off completely from the sample by a continuous flow of an inert gas. This takes some time and the continuously delivered volatiles need to be concentrated in a trap, either by absorption or by cold trapping. The trapped compounds are released from the trap by thermal desorption and transferred to the gas chromatograph. This technique, also known as *purge and trap*, is thus an off-line procedure, in contrast to the static headspace technique, where the headspace gas is transferred directly and on-line to the gas chromatograph. Thermal desorption is also used for sample transfer with a technique called *solid-phase microextraction* (SPME), where a thin rod or a small fibre, coated with a nonvolatile liquid phase, is inserted into a liquid sample or into the gas space of a headspace vial. The volatile compounds in the headspace are absorbed into the liquid-phase coating. After transfer into the heated injector of a gas chromatograph, the trapped compounds are released by thermal desorption. Off-line techniques, dynamic HS-GC and SPME are not discussed here, but all the important considerations regarding sample properties, such as matrix effects, necessary equilibration time, diffusion processes and sampling pretreatment, are common to all headspace techniques.

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Fundamentals of Static HS-GC

The theory of static HS-GC is best explained using the example of a liquid sample present in a closed vial, as shown in **Figure 1**. The volatile analyte present in the liquid sample will evaporate into the gas phase until the concentration in both phases (C_S and C_G) remain constant. Equilibrium is achieved by diffusion from the sample into the gas phase and vice versa. The equilibrium constant is called the partition coefficient (K), and can be split into the mass ratio (k) and the phase ratio (β).

The aim of every quantitative analysis is the determination of the original concentration of the analyte (C_0) in the sample. The peak area (A) in a headspace

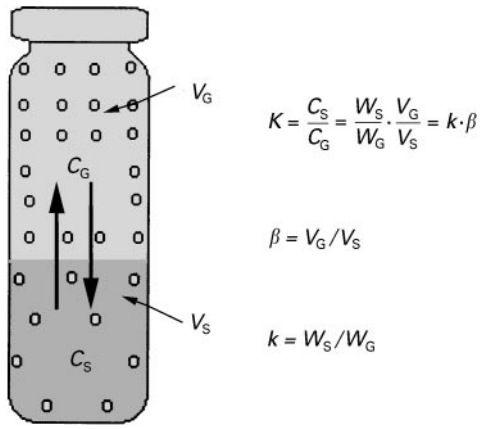

Figure 1 A headspace vial containing a liquid sample with a volatile analyte. Concentrations of the volatile analyte, C_G in the gas phase, C_S in the liquid phase; mass of the volatile analyte, W_G in the gas phase, W_S in the liquid phase; V_G, volume of the gas phase; V_S, volume of the liquid sample; K, partition coefficient; k, mass ratio; β, phase ratio.

chromatogram is proportional to the gas-phase concentration ($A \propto C_G$) and depends on the phase ratio (β). However, it depends not only on the sample volume (V_S), but also on the partition coefficient (K), as described by eqn [1]. This is the key relationship for static HS-GC:

$$C_G = \frac{C_0}{K + (V_G/V_S)} = \frac{C_0}{K + \beta} \qquad [1]$$

The partition coefficient depends on both the temperature and volume. These two parameters strongly influence headspace sensitivity and are conditions that can easily be selected by the operator.

Sensitivity of Static HS-GC

Influence of Sample Volume and Temperature on Headspace Sensitivity

The sample volume (V_S) is included in the phase ratio (β) in eqn [1], but its influence on headspace sensitivity is not independent of the partition coefficient (K). The latter can vary widely from practically zero in the case of a gas sample up to several thousands, where the applicability of HS-GC ends. The phase ratio (β), and thus the influence of the sample volume, does not generally span such a wide range. For example, a 1 mL sample in a 10 mL vial has a phase ratio of 9, while with a sample volume of 5 mL the phase ratio decreases to 1.

Whether or not this causes an increase in the resulting gas concentration, and thus of the resulting peak area, depends mainly on the partition coefficient. In the case of a high partition coefficient ($K >$ 100, e.g. ethanol in water), a change in the phase ratio from 1 to 5 will barely influence headspace sensitivity; in contrast, where the partition coefficient is very small the sensitivity increases in proportion to the sample volume (e.g. *n*-hexane in water at 50°C). This result may be surprising since it differs so much from normal GC analysis, where peak areas increase with increasing volumes of injected sample.

The vapour pressure of a compound increases exponentially with temperature. One would therefore expect a similar increase in the volatility, and thus enhanced sensitivity for a headspace compound. Again, however, there is a dependence on the partition coefficient. In the case of nonvolatile compound ($K \rightarrow \infty$), a higher temperature will not alter its nonvolatility. In the case of a highly volatile compound ($K \rightarrow 0$, already at room temperature), the temperature will not affect the headspace sensitivity either, because in this case nearly all of the compound is already present in the gas phase. Headspace samples generally fall between these two extremes. **Table 1** gives typical values of partition coefficients at three temperatures for three compounds with a small (tetrachloroethylene), a medium (ethyl acetate) and a high (ethanol) partition coefficient.

Sensitivity Enhancement by Matrix Modification

The partition coefficient can be altered by modifying the sample matrix. A common technique is the use of the *salting-out* effect. For aqueous samples with a high partition coefficient (e.g. ethanol in water), the addition of salt may enhance the sensitivity by up to a factor of 10. Again, the result depends on the value of the partition coefficient. In the case of a highly volatile compound ($K \rightarrow 0$), where nearly all of the analyte is already present in the gas phase, the sensitivity will not improve.

A similar effect is achieved with a sample containing a nonpolar volatile compound dissolved in a water-miscible organic solvent, such as dimethylacetamide, dimethylformamide, etc. If water is added to this solution, the solubility of the nonpolar compound will decrease and its volatility will increase.

Table 1 Partition coefficients (K) in water–air equilibrium system

Compound	*Temperature*		
	40°C	*60°C*	*80°C*
Tetrachloroethylene	1.5	1.3	0.9
Ethyl acetate	62.4	29.3	17.5
Ethanol	1355	511	216

Sensitivity Enhancement by Modifying the Volatile Analyte

Polar compounds, particularly those with an active hydrogen (alcohols, phenols, acids, amines, etc.), usually have low volatility as a result of intermolecular interaction with the polar matrix through hydrogen bond formation. However the reactivity of the active hydrogen can be used to prepare less polar derivatives with better volatility and lower solubility. Simple reactions are preferred, such as esterification, transesterification, acetylation, etc., which are carried out in the headspace vial during the equilibrium time. An advantage of HS-GC is that the reaction products are less polar and more volatile, thus shifting the equilibrium of the chemical reaction towards completeness.

Instrumentation for Headspace Sampling

All the devices that are commonly used for gas sampling may be applied to headspace analysis, including gas-tight syringes and gas-sampling valves. A particular problem in HS-GC is the internal pressure in the headspace vial that is generated during thermostatting at elevated temperature, represented by the sum of the partial vapour pressures of all the volatile compounds present, including water (since most samples contain some water). The vial must therefore be closed by a septum (preferably lined with polytetrafluoroethylene) (PTFE) and crimp-capped pressure-tight by an aluminium cap. This internal pressure may cause problems with sample loss during sample transfer with a gas syringe if it is not equipped with a pressure-tight valve. So that they can operate independently of the internal vial pressure, most automated headspace samplers surmount this problem by pressurizing the vial up to a certain pressure level above the original pressure prior to sample transfer. Although it is not possible here to describe the various commercially available instruments in detail, the common principle is shown schematically in **Figure 2**.

Inert carrier gas enters the gas chromatograph through valve V and branches before the column. Part of the gas is directed to the sampling needle N. If this needle penetrates the septum, carrier gas flows into the vial and pressurizes it, usually up to the column head pressure, but any other pressure may be applied. Sample transfer is subsequently performed by closing valve V for a short time (usually few seconds), thus disconnecting the gas supply. The pressurized headspace gas in the vial expands either through the sample loop of a gas-sampling valve to atmosphere or directly onto the column. This on-column headspace sampling (also known as balanced pressure sampling) has the advantage that no headspace gas is wasted by unnecessary expansion to atmosphere, allowing the application of cryofocusing enrichment techniques. The actual volume of the headspace gas and the amount of analyte in it can be calculated from the transfer time (seconds) during which valve V is closed and from the volume flow rate (mL s^{-1}) at the column head.

The carrier gas flow rate in a capillary column is much lower than in a packed column, and therefore a much smaller volume of the headspace gas is introduced during the same sampling time. The resulting lower sensitivity can be circumvented by an increased sampling time, provided the accompanying band-broadening is suppressed by the technique of cryofocusing (also called cryogenic trapping or cold trapping). The normal admissible sample volume in a capillary column is about 50–200 μL, which is only 1% of the usually available volume of 5–20 mL headspace gas in the vial. With this technique of splitless on-column headspace sampling it is possible to

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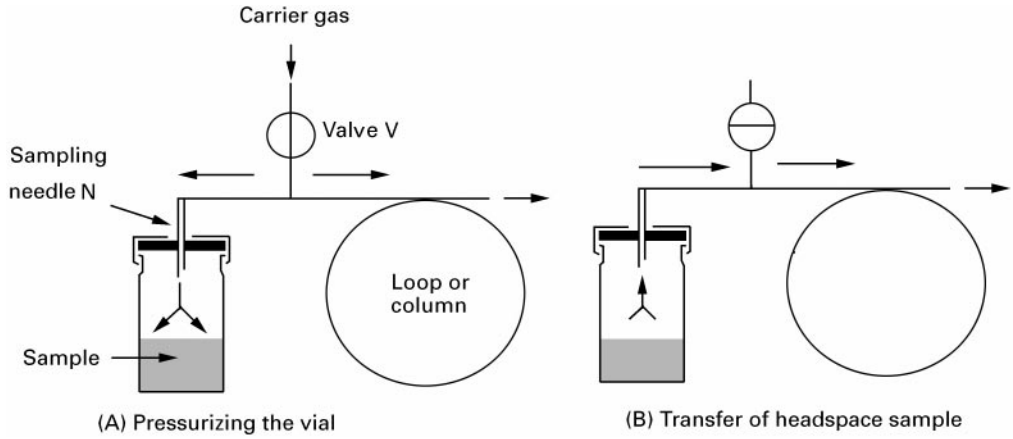

Figure 2 Principle of headspace sampling by either direct on-column sampling or by pressure/loop-filling with previous pressurization of the headspace vial.

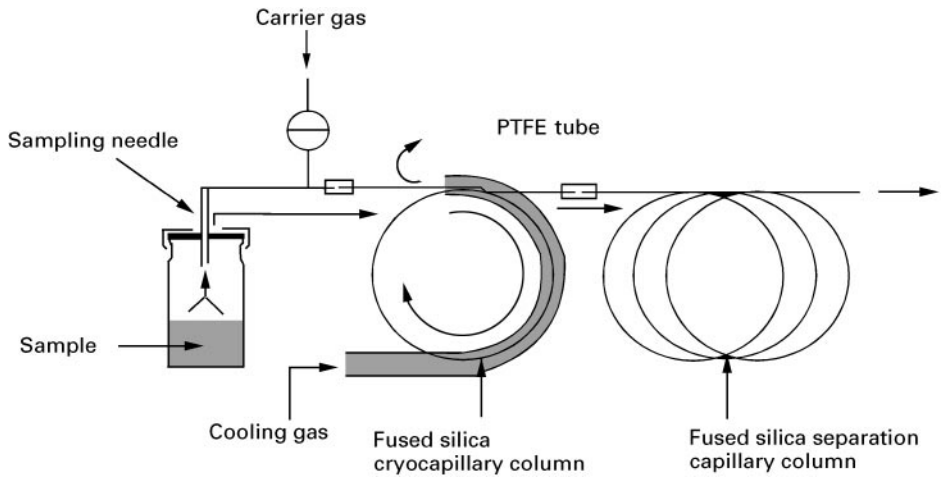

Figure 3 Principle of cryogenic headspace trapping with splitless on-column headspace sampling.

extend the sample transfer time from a few seconds up to several minutes with an accompanying increase in the headspace gas volume and sensitivity.

In the automated headspace sampler shown in **Figure 3** the cryotrap is placed in the oven of the gas chromatograph. The cryotrap is essentially a short piece of fused silica capillary column, either the first coil of the separation capillary or a corresponding short piece of a different capillary column. The latter, called here the cryocapillary column, is coated, preferably with dimethylsilicone, a substance with a glass transition temperature of $-114^{\circ}C$. Dimethylsilicone works as a stationary phase even at that low temperature, dissolving the compound in the liquid phase rather than just trapping by condensation. This cryocapillary column may then be connected to any other type of a capillary column by a butt connector. The cryocapillary column is jacketed by a 0.5 m PTFE tube, through which cold nitrogen gas flows outside the capillary column but in the opposite direction to the flow of warm carrier gas inside. The volatile analytes are trapped along the resulting strong temperature gradient in the capillary column. When sample transfer is interrupted by opening valve V, the flow of cooling gas is also stopped. A very rapid desorption is then achieved with a sharp starting band profile, since the warm carrier gas inside the capillary now heats the low mass fused silica capillary rapidly up to the oven temperature. The nitrogen gas used for cooling is produced outside the gas chromatograph by passing the nitrogen through a metal coil in a cooling bath, for example through liquid nitrogen. The sampling time and thus the headspace gas volume is restricted to only a few minutes before ice forms from the water sample, causing a blockage. However, a remarkable improvement of the sensitivity compared to the usual injection times of a few seconds is obtained. Injection times of up to 10 min can be obtained by placing in the sample transfer line a small trap containing lithium chloride on a solid support in a small tube. This water trap (optional and not shown in Figure 3) is regenerated after each analysis by heating to 200°C and backflushing the released water. The chromatogram in **Figure 4** gives an example of the headspace analysis of low ppb concentrations of volatile aromatic hydrocarbons (BTEX) in a water sample by cryo-HS-GC.

Quantitative Headspace Analysis

Any quantitative method used for HS-GC has to take into account the influence of the sample matrix. The neat matrix should be available to prepare calibration standards, except for gas samples or if the composition of the gas phase only has to be determined, as in aroma research. The calibration techniques of *standard addition* or *multiple headspace extraction* (MHE) do not need the pure sample matrix, as opposed to internal or external standard calibration, which do. A neat matrix is also not necessary if the volatiles are completely evaporated into the gas phase. This effect can be achieved by reducing the sample size in the vial to a very small amount – say 10–15 mg. The determination of phenols in a resin-coated copper wire is shown in **Figure 5** as an example for this technique, called *total vaporization* (TVT), or sometimes *full evaporation* (FET). The small amount of 10 mg in a 22.3 mL vial gives a phase ratio (β) of >2000 and thus a nearly exhaustive extraction, allowing calibration by an external vapour standard, prepared also by TVT.

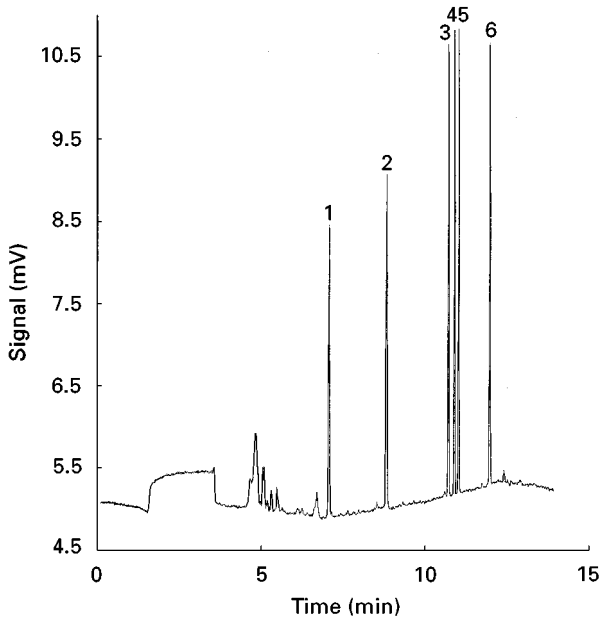

Figure 4 Determination of volatile aromatic hydrocarbons (BTEX) in water by cryo-HS-GC with FID. Perkin-Elmer AutoSystem, HS40 Automatic Headspace Sampler with cryoaccessory and water trap; cryocolumn: 0.8 m × 0.32 mm i.d. fused silica capillary, coated with immobilized dimethylsilicone, film thickness 1 μm; separation column: 60 m × 0.25 mm i.d., Stabilwax (Restek), film thickness 0.25 μm; temperature program: 40°C (1 min), 20°C min^{-1}, 65°C (4 min), 10°C min^{-1}, 100°C (8 min); carrier gas: He, 210 kPa; sampling: splitless 3 min; sample: 10 mL, equilibrated 35 min with shaker at + 80°C. Components: 1 μg L^{-1} each of: 1, benzene; 2, toluene; 3, ethylbenzene; 4, *p*-xylene; 5, *m*-xylene; 6, *o*-xylene.

Liquid samples are also accessible to this technique. In the case of solutions it is feasible to reduce the volume such that even the solvent evaporates completely at the appropriate temperature of the vial, without forming a condensed liquid phase, while nonvolatile sample constituents (e.g. salt in a wastewater sample or the polymer in the case of the polymer emulsion) remain as a dry residue in the vial. The admissible sample volume depends on the molar volume of the solvent and is typically about 15 μL in a 20 mL headspace vial. The vial is used here just as the glass liner in a normal GC injector, which retains the nonvolatile residue. An automated headspace sampler is thus used in a similar manner to an autosampler but with disposable injectors. This technique is very useful for samples that do not need the highest sensitivity; time-consuming equilibration is not required here and the volatile fraction of the sample is completely present in the gas phase. No matrix influence has to be calibrated and the quantitative analysis therefore is as simple as in normal GC.

However, HS-GC is, in general, applied to determine the volatile fraction of a sample and, except for normalization (which makes hardly any sense here), all other calibration methods may be applied. The principles behind these calibration methods for liquid samples are briefly discussed here; solid samples are treated below.

The use of an internal standard is the most popular calibration method in gas chromatography, but has some limitations for headspace analysis. A detector response factor must be determined, but if applied to HS-GC, matrix effects must also be included. A neat matrix must therefore be available to prepare a calibration standard. Such a calibration matrix may be prepared from the sample by stripping off all the volatiles first and spiking the remaining sample with the compounds to be analysed. Sometimes also an artificial matrix may be prepared (e.g. 11% ethanol in water, if flavour compounds in a wine sample are to be quantitated). If the sample is sufficiently concentrated it may be diluted with a (high boiling) solvent. This solvent then becomes a surrogate sample matrix because compounds below a concentration of about 1% usually have no measurable matrix effect. Sometimes an internal standard is added only to compensate for slight variations of the sample matrix. Since matrix effects are caused by intermolecular interaction, the internal standard should be of the same chemical nature as the compounds to be determined. For example, in blood alcohol analysis, another alcohol (*t*-butanol or *n*-propanol) is used. The main purpose of an internal standard calibration is to

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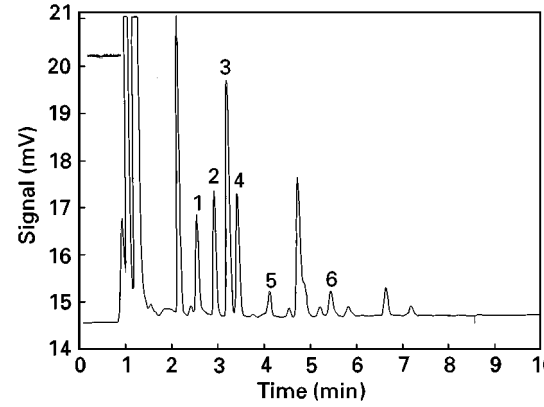

Figure 5 Determination of phenols from a resin-coated wire by TVT. Perkin-Elmer AutoSystem, HS40 Automatic Headspace Sampler; column: 25 m × 0.32 mm i.d. fused silica capillary, coated with immobilized poly(14% cyanopropylphenyl/86% dimethylsiloxane), film thickness 1 μm; temperature programme: 150°C (10 min), 10°C min^{-1}, 220°C; carrier gas: He, 118 kPa; split sampling: split flow 16 mL min^{-1}, sampling time: 0.08 min; detector: flame ionization (FID); headspace conditions: pressurizing gas (He), 145 kPa; needle and transfer line temperature, 200°C; sample, 10 mg, equilibrated 35 min at 210°C. Components: 1, phenol, 2.4% (w/w); 2, *o*-cresol; 3, 2,3-dimethylphenol; 4, *m*-cresol + *p*-cresol; 5, 2,4-dimethylphenol + 2,5-dimethylphenol; 6, 3,4-dimethylphenol.

compensate for poor sampling reproducibility. This may still be a problem with manual syringe injection, but not with autosamplers, whose sampling precision is in general $<1\%$.

External standard calibration also requires the neat matrix for preparing a standard sample, but permits simpler sample handling since no additional compounds need to be added to each sample. The sample is placed in the vial, which is closed immediately. The vial remains closed until an aliquot is withdrawn for analysis, thus guaranteeing sample integrity. This is the most simple calibration technique.

If a neat matrix sample is not available, then the method of standard addition is the most universal calibration method. Calibration is carried out with each analyte and no response factor is necessary. The added compound suffers the same matrix effects as the original sample. Standard addition needs at least two analyses to be carried out for each sample, but the increased time required is less of a disadvantage if an automated headspace sampler is used. Several repeated determinations are necessary in any case if statistical confirmation of the analytical result is required, preferably by multilevel addition with linear regression calculation of the result.

Another technique that does not need the neat sample matrix uses repeated gas extractions. This is similar to the dynamic headspace technique, with the difference that the volatiles are removed by a stepwise gas extraction rather than continuously. This technique of multiple headspace extraction (MHE) can be carried out with the same instrumentation as used for static HS-GC. With the technique of direct on-column headspace sampling it is carried out in such a way that the vial is first pressurized as described above. When sample injection is stopped, the vial is pressurized again, but its gas phase subsequently vented to the atmosphere. Thus most of the headspace gas is removed, depending on the ratio of headspace pressure (P_H) to atmospheric pressure (P_A). The equilibrium is disturbed, since the gas-phase concentration (C_G) has dropped. The equilibrium has to be re-established by additional evaporation of the analyte and the next analysis now gives a smaller peak, the difference corresponding to the amount of the analyte vented.

This stepwise gas extraction analysis is repeated several times and a series of exponentially decreasing peak areas is obtained. The logarithm of the peak area is plotted against the number of extractions, to give a straight line that allows the application of linear regression to obtain the sum of the area values as the sum of a geometric progression. It is not necessary to proceed until exhaustive extraction is achieved, since a minimum of two area values allows such a linear regression calculation. The total area obtained corresponds to the total amount of the analyte in the sample and this value is independent of the matrix influence. The resulting area total must be calibrated, but for this purpose the matrix is not required, and even a vapour standard, prepared very conveniently by the TVT technique, can be used as an external standard. In practice it is the gas phase concentrations in both vials that are compared. A correction for the sample volume is therefore necessary, since the volume of the gas phase in the vial containing the sample differs by the sample volume in comparison to the 'empty' calibration vial, and so does the corresponding concentration in the gas phase.

Classification of Sample Types

All of the calibration techniques described above may be applied to liquid samples with no particular problems. Sometimes it is necessary to dilute very viscous samples or to reduce long equilibration times by using a shaker. Liquid samples also show a wide range of linear relationships between concentration in the sample and peak area – the headspace linearity. Solid samples can also be analysed by HS-GC, but only if they behave as a partition system, similar to liquid samples, owing to inherent calibration problems. However, most solid samples behave as a nonlinear adsorbent. Additional problems are caused by slow diffusion in a solid matrix; size, porosity and specific surface of solid samples are therefore very important parameters. Bulky solid samples are not amenable to HS-GC at all unless they are pulverized, for example by freeze grinding, with loss of the volatiles avoided by chilling the sample with liquid nitrogen or dry ice. There are many problems to be taken into account and most techniques for solid samples try to establish a partition system, which can then be treated like a liquid sample.

Polymers and plastic materials often behave as partition systems if heated above the glass transition temperature. A classical example is the determination of vinyl chloride monomer in a polyvinyl chloride (PVC) resin above the glass transition temperature of 85°C. Such solid samples can be handled as a quasiliquid sample with all types of calibration techniques. Even the technique of standard addition may be applied, because the analyte may be added to the gas phase and not necessarily into the sample using the existing equilibrium system to achieve homogeneous partitioning from both directions. However, considering the variety of plastic materials – pure resins, preforms, copolymers, complex mixtures with all type of additives and finished products – any new solid sample has to be checked carefully for this

property. An example for a systematic approach to develop a suitable quantitative method for a solid sample is given below.

The most common procedure for headspace analysis of solids is the *solution approach*, where the sample is dissolved in an appropriate high boiling solvent, which is eluted late in the chromatogram and may be removed by column backflushing. The disadvantage is the reduced sensitivity due to the dissolution.

Insoluble samples can often be handled as a suspension in water or an organic solvent, using the displacement effect of the solvent. This *suspension approach* works well where the analytes are superficially adsorbed. It is obvious that the samples should be a powder rather than a bulky material, to provide the necessary large surface. Calibration in this case is straightforward by using an external standard in the same solvent. The insoluble solid sample remains as a slurry in the headspace vial and causes no matrix effect. A smaller amount of solvent is sufficient here to dissolve only the displaced volatiles, compared to the solution approach where the whole sample must be dissolved. But the resulting smaller dilution effect may be even further minimized by reducing the volume of the high boiling solvent such that only the surface of the sample is wetted by the solvent, which then works as a surface modifier. This *surface modification* technique provides a homogeneous surface with constant adsorptivity. In this way a much better sensitivity can be achieved owing to the smaller amount of such a liquid displacer. The absence of any residual adsorptivity, however, has to be confirmed, e.g. by the MHE technique. In this case the solid sample with its homogeneous surface behaves like a partition system, where the partition coefficient remains constant over a wide range.

Practical Example: Determination of Ethylene Oxide in a PVC Tube

From the foregoing discussion it is apparent that there are several possible ways to carry out a quantitative headspace analysis. A systematic approach to develop the most suitable calibration technique is therefore desirable. This is illustrated by the following example of the determination of ethylene oxide (EO) in a sterilized PVC tube. Ethylene oxide is widely used for sterilization, but due to its toxicity the residual concentration must be carefully controlled down to a safe limit (e.g. 1 ppm). This example covers several of the aspects discussed above. Since PVC tubing is a solid sample, the solution approach was naturally the first choice. The sample was dissolved in dimethylacetamide and calibration was by multilevel standard addition (see **Figure 6**), resulting in an EO concentration of 19.95 ppm with a precision as expressed by the correlation coefficient of 0.9961.

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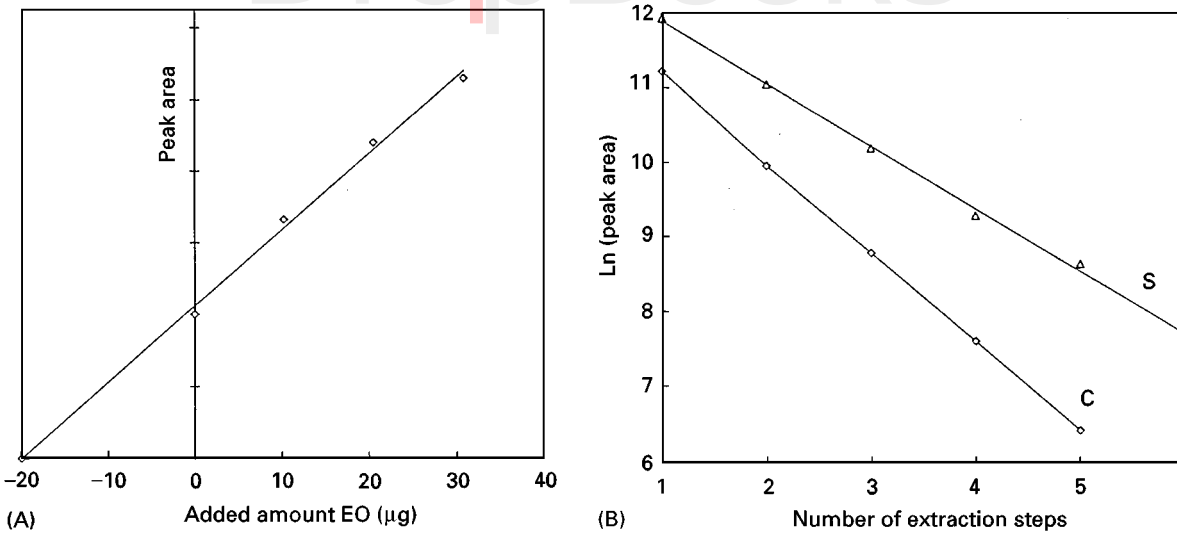

Figure 6 Determination of EO in a sterilized PVC tube by standard addition calibration (STA) and by multiple headspace extraction (MHE). Gas chromatographic conditions: Perkin-Elmer SIGMA 2000, HS100 Automatic Headspace Sampler; 2 m × 3.2 mm stainless steel column, packed with Chromosorb 101, 80/100 mesh; temperature programme: 100°C (7.5 min), 15°C min^{-1}, 200°C; detector: FID; carrier gas: He, 20 mL min^{-1}; calibration standard: aqueous solution of EO (10.3 μg $μL^{-1}$).
(A) STA. Sample preparation: 1 g PVC tube, dissolved in 2 mL dimethyl acetamide, equilibrated 90 min at 90°C; calibration by adding 10, 20 and 30 μL of the calibration standard; result: 19.95 μg g^{-1} EO, regression coefficient $r = 0.9961$.
(B) MHE. Sample preparation: 1 g PVC tube, cut in pieces of 3 mm × 4 mm, 1 mm thick, equilibrated as above; calibration by external vapour standard, prepared by TVT of 8 μL; total area counts from sample analysis: 258 464, from calibration standard: 104 132; result: 19.53 μg g^{-1} EO; regression coefficients: sample (S), $r = -0.99914$; calibration standard (C), $r = -0.99990$.

Due to problems with solvent impurities and also to achieve a better sensitivity, a solvent-free method was expected to be superior. A six-step MHE procedure with the sliced solid sample was calibrated with a five-step MHE of an external vapour standard (see Figure 6) and after the necessary volume correction a nearly identical concentration of 19.53 ppm was obtained, but now with a four-times higher sensitivity. Also the precision was better, as expressed by the linear regression coefficients of -0.99914 for the sample and -0.99990 for the calibration standard. This allowed reduction of the MHE procedure to three steps, but still with a linear regression calculation, and a two-step procedure is sufficient if the highest precision is not required.

From these good results some more conclusions may be drawn to simplify the analysis further. The good linearity over the whole working range indicated that the solid PVC matrix was behaving as a partition system; this conclusion allowed the application of standard addition calibration in the form of gas-phase addition. Even the use of an internal standard appears feasible, since from a successful gas-phase addition it can be concluded not only that EO partitions between both phases, but that any other compound will do the same, provided it is similar in its chemical properties (e.g. dimethyl ether). As discussed above, a calibration factor has to be determined first, which comprises not only the differences in the detector response but also the different solubilities (partition coefficients) in the PVC matrix. For this example it is no problem to obtain a PVC tube without any EO in it.

Taking into account all these possibilities, the final decision as to what is a suitable calibration technique may depend on other considerations such as the simplicity of sample handling or the sample throughput in an automated headspace sampler. For example, the standard addition calibration needs a series of vials to be subsequently analysed, thus occupying the corresponding number of places in the turntable of an autosampler, while for the MHE procedure the determinations are all carried out from the same vial and the sample throughput in an autosampler will therefore not be affected. On the other hand, the addition of an internal standard to every sample is tedious and prone to errors, particularly if pipettes are used to transfer solutions with highly volatile compounds.

Applications

Static HS-GC relies in general on a thermodynamically controlled equilibrium. It is natural therefore that it has been applied not only for analytical purposes, but also for the determination of physicochemical data such as vapour pressures, partition coefficients, activity coefficients and related mixing functions (energies and enthalpies of mixing), adsorption isotherms, and also for kinetic measurements such as the determination of reaction constants and the rate of release of volatile compounds from solid material. **Table 2** lists some important analytical applications.

Table 2 Selected analytical applications of static headspace gas chromatography

- Residual solvents in pharmaceuticals, food, packing material, aluminium and plastic films
- Monomers in polymer resins, emulsions and finished products
- Ethylene oxide in sterilized clinical material
- Volatile aromatic and halogenated hydrocarbons in air, water and soil
- Flavour compounds in beverages and spices
- Odour compounds in foodstuffs, herbs, flowers and perfumes
- Rancidity of fat and oil
- Water content in any type of liquid and solid sample as an alternative to KF titration
- Dithiocarbamates, degraded to CS_2, in vegetables, fruits and flowers
- Analysis of beverages for diketones (in beer), sulfur compounds, alcohols, esters, aldehydes and acids
- Ethanol in blood, food and beverages
- Volatile fermentation products from anaerobic bacteria

See also: **II/Chromatography: Gas:** Column Technology; Historical Developments; Sampling Systems; Theory of Gas Chromatography. **III/Gas Analysis: Gas Chromatography**.

Further Reading

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